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JAPANESE PATENT NO. HEI 11[1999]-158358
CALENDERABLE POLYESTER ELASTOMER COMPOSITION

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(57) Abstract
Task

To provide calenderable polyester elastomer compositions having a good balance of calender processability and weather resistance, and producing sheets and films having excellent surface appearance, mechanical properties, heat resistance, and color.

Means for solution

Compositions consisting of (A) 100 parts by weight of a polyester elastomer containing mainly a high-melting crystalline polymer segment and low-melting polymer segment made from an aliphatic polyether unit and/or an aliphatic polyester unit and (B) 0.001-10 parts by weight of a hindered amine compound with a melting point above 90°C specified by JIS K0064, or with the hindered amine compound (B) added in combination with 0.001-10 parts by weight each of (C) hindered phenol compounds, (D) phosphite compounds and/or thiophosphite compounds, and (E) one more substance chosen from benzotriazole compounds, benzophenol compounds, and benzoate UV absorbers.

Claims

1. Calenderable polyester elastomer composition consisting of (A) 100 parts by weight of a polyester elastomer containing mainly a high-melting crystalline polymer segment and low-melting polymer segment made from an aliphatic polyether unit and/or an aliphatic polyester unit and (B) 0.001-10 parts by weight of a hindered amine compound with a melting point above 90°C specified by JIS K0064.

2. Calenderable polyester elastomer composition consisting of (A) 100 parts by weight of a polyester elastomer containing mainly a high-melting crystalline polymer segment and low-melting polymer segment made from an aliphatic polyether unit and/or an aliphatic polyester unit, (B) 0.001-10 parts by weight each of a hindered amine compound with a melting point above 90°C specified by JIS K0064, and (C) a hindered phenol compound.

3. Calenderable polyester elastomer composition consisting of (A) 100 parts by weight of a polyester elastomer containing mainly a high-melting crystalline polymer segment and a low-melting polymer segment made from an aliphatic polyether unit and/or an aliphatic polyester unit, (B) 0.001-10 parts by weight each of a hindered amine compound with a melting point above 90°C specified by JIS K0064, (C) a hindered phenol compound, and (D) a phosphite compound and/or thiophosphite compound.

4. Calenderable polyester elastomer composition consisting of (A) 100 parts by weight of a polyester elastomer containing mainly a high-melting crystalline polymer segment and a low-melting polymer segment made from an aliphatic polyether unit and/or an aliphatic polyester unit, 0.001-10 parts by weight each of (B) a hindered amine compound with a melting point

above 90°C specified by JIS K0064, (C) a hindered phenol compound, (D) a phosphite compound and/or thiophosphite compound, and (E) one or more substances chosen from benzotriazole compounds, benzophenone compounds, and benzoate UV absorbers.

5. Calenderable polyester elastomer composition obtained by the further addition of processing aids to any of the compositions described in Claims 1-4.

6. Calenderable polyester elastomer composition described in Claim 5, wherein the processing aid is a polyolefin wax and/or fluororesin.

Detailed explanation of the invention

[0001]

Technological field of the invention

The present invention concerns calenderable polyester elastomer compositions having a good balance of calender processability and weather resistance, and producing sheets and films having excellent surface appearance, mechanical properties, heat resistance, and color.

[0002]

Conventional technology

Polyester block copolymers containing mainly a high-melting crystalline polymer segment and a low-melting polymer segment made from an aliphatic polyether unit and/or an aliphatic polyester unit are known to have rubbery elasticity and have been widely used as so-called polyester elastomers in fibers, films, molded products, etc.

[0003]

However, due to the presence of the low-melting polymer segment in the main chain, polyester elastomer products easily suffer oxidative degradation, leading to a reduced degree of polymerization and mechanical properties as well as surface cracks in molded products, discoloration, etc., which are not favorable phenomena. In particular, the oxidative degradation is accelerated by light, heat, etc., thus their applications outdoors and at high temperatures are rather limited.

[0004]

Conventionally, to counter these problems, there have been many attempts to improve the weather resistance of polyester elastomers. For example, polyester elastomers are compounded with hindered phenol compounds, phosphite compounds, and hindered amine compounds in certain amounts (Japanese Kokoku Patent No. HEI 2[1990]-12982), or polyester elastomers are compounded with hindered phenol compounds, phosphite compounds, and thiophosphite compounds in certain amounts (Japanese Kokoku Patent No. SHO 62[1987]-14179).

[0005]

Calender processing is widely used for efficiently making sheets and films, and this calender processing has also been practiced for polyester elastomers. However, conventional polyester elastomer compositions disclosed in Japanese Kokoku Patent Nos. HEI 2[1990]-12982 and SHO 62[1987]-14179 have definitely improved the weather resistance and heat resistance, but in calender processing, because of the compounds added, sticking of polyester elastomer compositions to the calender roll increases, and in some cases calender molding is not possible at all.

[0006]

Problems to be solved by the invention

It is an objective of the present invention to provide calenderable polyester elastomer compositions having a good balance of calender processability and weather resistance, and producing sheets and films having excellent surface appearance, mechanical properties, heat resistance and color.

[0007]

Means for solving the problems

As an intense investigation of such problems, we have discovered that polyester elastomers compounded with a certain amount of hindered amine compounds with melting points exceeding a certain temperature, or hindered amine compounds with melting points exceeding a certain temperature together with hindered phenol compounds, phosphite compounds, and/or thiophosphite compounds, along with one or more substances chosen from benzotriazole compounds, benzophenone compounds, and benzoate UV absorbers, show improvements in both calender processability and weather resistance. Thus, the present invention is attained.

[0008]

Namely, the calenderable polyester elastomer compositions of the present invention are characterized by consisting of (A) 100 parts by weight of a polyester elastomer containing mainly a high-melting crystalline polymer segment and a low-melting polymer segment made from an aliphatic polyether unit and/or an aliphatic polyester unit and (B) 0.001-10 parts by weight of a hindered amine compound with a melting point above 90°C specified by JIS K0064.

[0009]

The calenderable polyester elastomer compositions also include those in which the hindered amine compounds are added in combination with 0.001-10 parts by weight each of (C) hindered phenol compounds, (D) phosphite compounds and/or thiophosphite compounds, and (E) one or more substances chosen from benzotriazole compounds, benzophenone compounds, and benzoate UV absorbers, with the combination being (B)/(C), (B)/(C)/(D), or (B)/(C)/(D)/(E).

[0010]

Furthermore, in addition to such additives, the calenderable polyester elastomer compositions may also contain processing aids such as polyolefin waxes, fluororesins, etc. With the hindered amine compounds having melting points above 90°C in the calenderable polyester elastomer compositions of the present invention, the calender processability is greatly improved while a high weather resistance is maintained.

[0011]

Practical embodiments of the invention

The polyester elastomers (A) used in the present invention are block copolymers consisting of mainly a high-melting crystalline segment and low-melting polymer segment made of an aliphatic polyether unit and/or aliphatic polyester unit.

[0012]

The high-melting crystalline polymer segment of polyester elastomer (A) is mainly a polyester hard segment. The dicarboxylic acid component forming such a polyester hard segment may be aromatic dicarboxylic acids such as terephthalic acid, isophthalic acid, phthalic acid, 2,6- or 1,6-naphthalenedicarboxylic acid, 4,4'-diphenyl ether dicarboxylic acid, etc.; alicyclic dicarboxylic acids such as 1,4-cyclohexanedicarboxylic acid, cyclopentanedicarboxylic acid, etc.; aliphatic dicarboxylic acids such as adipic acid, sebacic acid, azelaic acid, etc., while aromatic dicarboxylic acids are preferred, and the use of terephthalic acid is especially recommended.

[0013]

The diol components used for forming polyether hard segments may be C₂₋₁₂ aliphatic or alicyclic diols, e.g., ethylene glycol, propylene glycol, 1,4-butanediol, neopentyl glycol, 1,5-pentanediol, 1,6-hexanediol, decamethylene glycol, cyclohexanedimethanol, bisphenols such as bis(p-hydroxyphenyl)biphenyl, bis(p-hydroxyphenyl)methane, bis(p-hydroxyphenyl)propane, etc., or mixtures thereof, while C₂₋₈ aliphatic or alicyclic diols are especially preferred.

[0014]

The aliphatic polyether unit in the soft segment of polyester elastomer (A) may be polyethylene glycol, poly(1,3- or 1,2-propylene) glycol, poly(tetramethylene oxide) glycol, polyethylene glycol-polypropylene glycol block copolymer, polyethylene glycol-poly(tetramethylene oxide) glycol block or random copolymer, etc., while poly(tetramethylene oxide) glycol with an average molecular weight of about 200-6000 is preferred.

[0015]

The aliphatic polyester unit in the soft segment of polyester elastomer (A) may be poly-ε-caprolactone, polyenantlactone [transliteration], polycaprylolactone, polybutylene adipate, polyethylene adipate, etc., while poly-ε-caprolactone and polybutylene adipate are preferred.

[0016]

The polyester elastomers (A) may be prepared by any method. In an example of a suitable polymerization method, a dicarboxylic acid diester is heated together a low-molecular-weight glycol and poly(alkylene oxide) glycol in an excess amount (about 1.2-2.0 times the moles of the acid) in the presence of an ordinary esterification catalyst at about 150-200°C under ambient pressure with the distillation of methanol for an ester-exchange reaction, then polymerized at 200-270°C under a vacuum of 5 mm Hg or below.

[0017]

In the present invention, it is important that the hindered amine compounds (B) have a melting point above 90°C as specified by JIS K0064. Specific examples of compounds satisfying such a requirement are bis (1,2,2,6,6-pentamethyl-4-piperidyl) 2-(3,5-di-t-butyl-4-hydroxybenzyl)-2-butylmalonate (Tinuvin 144), tetrakis(2,2,6,6-tetramethyl-4-piperidyl) 1,2,3,4-butanetetracarboxylate, N,N'-bis(3-aminopropyl)ethylenediamine, 2,4-bis[N-butyl-N-(1,2,2,6,6-pentamethyl-4-piperidyl)amino]-6-chloro-1,3,5-triazine condensate (Chimassorb [transliteration] 119), 1-[2-[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionyloxy]ethyl]-4-[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionyloxy]-2,2,6,6-tetramethylpiperidine (Sanol LS-2626), dimethyl succinate-1-(2-hydroxyethyl)-4-hydroxy-2,2,6,6-tetramethylpiperidine polycondensate (Tinuvin 622 LD), poly[(6-(1,1,3,3-tetramethylbutyl)amino-1,3,5-triazin-2,4-diyl){(2,2,6,6-tetramethyl-4-piperidyl)imino}hexamethylene{(2,2,6,6-tetramethyl-4-piperidyl)imino}] (Chimassorb 944), etc.

[0018]

With hindered amine compounds (B) having melting points below 90°C, e.g., bis(2,2,6,6-tetramethyl-4-piperidyl) sebacate with a melting point of 81-85°C, improved weather resistance is obtained, but the calender processability is not improved, thus not favored. The amount of the hindered amine compounds (B) added should be 0.001-10 parts by weight, especially 0.01-5 parts by weight, to 100 parts by weight of polyester elastomer (A). Below 0.001 part by weight, the desired improvements in weather resistance and calender processability are not obtained, while above 10 parts by weight, the additive blooms over the calendered sheet surface, giving a poor appearance.

[0019]

The calenderable polyester elastomer compositions of the present invention compounded with the hindered amine compounds (B) as well as hindered phenol compounds (C) show synergetic improvements in weather resistance and heat resistance.

[0020]

The hindered phenol compounds (C) that can be used in the present invention may be n-octadecyl 3-(3',5'-di-t-butyl-4'-hydroxyphenyl)propionate, 6-(4-hydroxy-3,5-di-t-butylanilino)-2,4-bis(octylthio)-1,3,5-triazine, hexamethylene glycol bis[β-(3,5-di-t-butyl-4-

hydroxyphenyl)propionate], N,N'-hexamethylenebis(3,5-di-t-butyl-4-hydroxyhydrocinnamide), 2,2'-thio[diethyl-bis-3(3,5-di-t-butyl-4-hydroxyphenyl)propionate], 3,5-di-t-butyl-4-hydroxybenzylphosphonic acid octadecyl ester, tetrakis[methylene-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate]methane, 1,3,5-trimethyl-2,4,6-tris(3,5-di-t-butyl-4-hydroxybenzyl)benzene, 1,1,3-tris(2-methyl-4-hydroxy-5-t-butylphenyl)butane, tris(3,5-di-t-butyl-4-hydroxyphenyl) isocyanurate, tris[β -(3,5-di-t-butyl-4-hydroxyphenyl)propionyloxyethyl] isocyanurate, etc., while those having molecular weights above 500 are highly effective, with no evaporation at high temperatures.

[0021]

The amount of hindered phenol compounds (C) added should be 0.001-10 parts by weight, preferably 0.01-5 parts by weight, to 100 parts by weight of polyester elastomer (A). Below 0.001 part by weight, the desired synergetic effects cannot be obtained, while above 10 parts by weight, the additives bloom over the calendered sheet surface, giving a poor appearance, thus not favored.

[0022]

In the present invention, the calenderable polyester elastomer compositions compounded with the hindered amine compounds (B) and hindered phenol compounds (C) as well as phosphite compounds and/or thiophosphite compounds (D) show synergetic improvements in calender processability, weather resistance, and heat resistance.

[0023]

The phosphite compounds that can be used in the present invention may be tributyl phosphite, trihexyl phosphite, trioctyl phosphite, trinonyl phosphite, tridecyl phosphite, trioctadecyl phosphite, triphenyl phosphite, tricresyl phosphite, tris(nonylphenyl) phosphite, tris(octylphenyl) phosphite, diphenyl decyl phosphite, diphenyl dodecyl phosphite, diphenyl stearyl phosphite, etc.

[0024]

The thiophosphite compounds that can be used in the present invention may be trinonyl trithiophosphite, trilauryl trithiophosphite, tristearyl trithiophosphite, triphenyl trithiophosphite, tris(p-nonylphenyl) trithiophosphite, tris(p-laurylphenyl) trithiophosphite, tris(2-lauryloxycarbonyl) trithiophosphite, tris(p-benzoyloxycarbonylbenzyl) trithiophosphite, tris[2-(p-laurylphenoxy)carbonyl] trithiophosphite, etc.

[0025]

The amount of phosphite compounds and/or thiophosphite compounds (D) added should be 0.001-10 parts by weight, preferably 0.01-5 parts by weight, to 100 parts by weight of polyester elastomer (A). Below 0.001 part by weight, the desired synergetic effects cannot be

obtained, while above 10 parts by weight, the additives bloom over the calendered sheet surface, giving a poor appearance, thus not favored.

[0026]

In the present invention, the calenderable polyester elastomer compositions compounded with the hindered amine compounds (B), hindered phenol compounds (C), and phosphite compounds and/or thiophosphite compounds (D) as well as one or more compounds (E) selected from benzotriazole compounds, benzophenone compounds, and benzoate UV absorbers, show synergetic improvements in calender processability, weather resistance, and heat resistance.

[0027]

The benzotriazole compounds that can be used in the present invention may be 2-(2-hydroxy-3-t-butyl-5-methylphenyl)-5-chlorobenzotriazole, 2-(2-hydroxy-3,5-di-t-butylphenyl)-5-chlorobenzotriazole, 2-(2-hydroxy-5-methylphenyl)benzotriazole, 2-(2-hydroxy-3-t-butyl-5-methylphenyl)benzotriazole, 2-(2-hydroxy-3,5-di-t-butylphenyl)triazole, etc.

[0028]

The benzophenone compounds that can be used in the present invention may be 2-hydroxy-4-n-octyloxybenzophenone, 2-hydroxy-4-n-lauryloxybenzophenone, 2-hydroxy-4-n-stearyloxybenzophenone, 2-hydroxy-4-n-octyloxy-4'-chlorobenzophenone, 2-hydroxy-4-n-octyloxy-3',4'-dichlorobenzophenone, etc.

[0029]

The benzoate UV stabilizers that can be used in the present invention may be 2,4-di-t-butylphenyl -3',5'-di-t-butyl-4'-hydroxybenzoate, phenyl salicylate, or 4-t-butylphenyl salicylate. The amount of at least one compound (E) chosen from benzotriazole compounds, benzophenone compounds, and benzoate UV absorbers added should be 0.001-10 parts by weight, preferably 0.01-5 parts by weight, to 100 parts by weight of polyester elastomer (A). Below 0.001 part by weight, the desired synergetic effects cannot be obtained, while above 10 parts by weight, the additives bloom over the calendered sheet surface, giving a poor appearance, thus not favored.

[0030]

The calenderable polyester elastomer compositions of the present invention can be obtained by adding the additives at any time during or after polyester elastomer polymerization, while adding the additives after polymerization (but before molding) is most desirable. In the preparation of the calenderable polyester elastomer compositions of the present invention, other ordinary additives such as processing aids, hydrolysis improving agents, colorants (pigments, dyes), antistatic agents, conductive agents, nucleating agents, lubricants, fillers, reinforcements, adhesion promoters, plasticizers, release agents, fire retardants, etc., may also be compounded, if they have no adverse effects on the desired properties. Calender processability can be further

improved by adding a certain amount of processing aids chosen from polyolefin waxes and/or fluororesins such as polytetrafluoroethylene, ethylene-fluoroethylene copolymer, polyvinylidene fluoride, etc.

[0031]

Examples

In the examples given below, % and parts are wt% and parts by weight unless specified otherwise. Property values given in the examples are measured by the methods given below.

Melting point: Measured by DSC method according to JIS K0064.

[0032]

Hardness: Shore D scale value measured according to JIS K7215.

Melt viscosity index: MFR value measured at 200°C and with a 2160-g load according to ASTM D1238.

[0033]

Calender processability: In an 8-inch, 2 roll system of the Nippon Roll Co., a polyester elastomer that is dry blended with additives or pellets obtained by melt mixing is added to the roll, and the time needed to stick to the roll (roll lubricity retention time) is measured.

[0034]

Sheet peelability from the roll after 20 min is evaluated in the 5 grades shown below.

- 5 Peelable without resistance, comparable to the case of polyvinyl chloride.
- 4 Somewhat inferior to 5, but the peelability is good.
- 3 Peelability is poor and not satisfactory for mass production
- 2 Peelability is poor; calender processing is difficult
- 1 No peeling at all

Similarly, the plate-out property is evaluated in 5 grades.

[0035]

- 5 Good (no plate-out visible even after calendaring for more than 50 min)
- 4 Somewhat good
- 3 Fair (calender-processable)
- 2 Calender processing difficult
- 1 Calender processing practically impossible

Molding appearance: Visual evaluation of the surface of a 0.5-mm-thick calender sheet.

[0036]

Weather resistance: A JIS (No. 2) 45% test piece punched from the above 0.5-mm-thick calender sheet is irradiated in a sunshine weatherometer; the time until surface crack formation is measured. In the sunshine weatherometer, the temperature is 63°C and water is sprayed for 18 min every 2 h.

[0037]

Heat resistance: A JIS (No. 2) 45% test piece punched from the above 0.5-mm-thick calender sheet is aged in a gear oven at 140°C; the time needed to lose one-half of the initial elongation at break is measured.

Reference Example 1

Polymerization of polyester elastomer (A-1)

In a reactor fitted with a helical ribbon stirring blade, 194 parts of dimethyl terephthalate, 265.4 parts of poly(tetramethylene oxide) glycol with a number-average molecular weight of 100, 69.6 parts of tetramethylene glycol, and 0.10 part of titanium tetrabutoxide were heated at 190-225°C for 2 h with the distillation of 95% of the theoretical amount of methanol.

[0038]

The reaction mixture was treated with 0.5 part of Irganox 1010 (hindered phenol type of heat stabilizer, product of CIBA-GEIGY Co.), then heated to 245°C; the interior pressure was reduced to 0.2 mm Hg over a period of 50 min, and the polymerization continued under the same conditions for 2 h. The polymer formed was extruded into a strand into water and cut into pellets to obtain polymer A-1.

[0039]

Reference Example 2

Polymerization of polyester elastomer (A-2)

In a reactor fitted with a helical ribbon stirring blade and a distillation tower, 100 parts of terephthalic acid, 110 parts of 1,4-butanediol, and 0.10 part of titanium tetrabutoxide were stirred, with the distillation of water formed by the reaction for esterification in a nitrogen atmosphere under ambient pressure for 2 h. The reaction product was transferred into a polymerization vessel and heated at 250°C and 0.2 mm Hg for 2 h for polymerization. The polymer formed was extruded into a strand into water and cut into pellets to obtain polybutylene terephthalate having a relative viscosity of 1.47 and melting point of 225°C.

[0040]

This polybutylene terephthalate and ϵ -caprolactone were fed at 900 g/h and 1700 g/h, respectively, into the feed opening at the back end of a single-screw extruder having a 200-mm-long kneading unit in the middle and front parts, inner diameter 30 mm ϕ and $L/D = 40$, cylinder middle-part temperature 240°C, and screw rotation 30 rpm.

[0041]

The polymer formed was extruded through a die in a strand form and cut to obtain pellets. In a vented single full-flight screw extruder with an inner diameter of 30 mm ϕ and $L/D = 40$, 100 parts of the pellets and 0.1 part of triphenyl phosphite were kneaded at a vent vacuum of 10 mm Hg, extrusion temperature of 200°C and screw rotation of 60 rpm for ϵ -caprolactone

removal and catalyst deactivation. The polymer was extruded in a strand form through a die and cut into pellets to obtain polymer A-2.

[0042]

Compositions and properties of the polyester elastomers A-1 and A-2 are given in Table 1.

[0043]

Table 1

Table 1

Polyester elastomer	Copolymerized poly(tetramethylene oxide) glycol amount (wt%)	Copolymerized polycaprolactone amount (wt%)	Melting point (°C)	Shore D hardness	Melt viscosity index (g/10 min)
A-1	65		165	38	8
A-2		65	171	39	26

[0044]

Application Examples 1-9

Polyester elastomer A-1 obtained in Reference Example 1 was dry blended with hindered amine compounds B-1~B-4 shown in Table 2 and a lubricant; the resulting compositions were fed into a calender molding machine at a roll temperature of 165°C and formed into sheets (Application Examples 1-4).

[0045]

The hindered amine compound was used together with the hindered phenol compound (C-1) shown in Table 3 (Application Example 5); hindered phenol compounds (C-1~C-2) and phosphite compound (D-1) (Application Examples 6-7); hindered phenol compounds (C-1~C-2), phosphite compound or thiophosphite compound (D-1~D-2), benzophenone compound, and benzotriazole compound (E-1~E-2) (Application Examples 8-9) to obtain calender sheets.

[0046]

Each additive was added to 100 parts of the polyester elastomer at 0.3 part, and 0.6 part of polyethylene wax (Hiwax 2203A, product of Mitsui Petrochemical Co.) was added as a processing aid. Evaluation results for each are given in Table 4.

Comparative Examples 1-7

Calender sheets were obtained similarly as in Application Example 1 with polyester elastomer A-1 and without the addition of the additives B-E at all. Results of the sheet property evaluation are given in Table 4 as Comparative Example 1.

[0047]

Polyester elastomer A-1 compounded with the same amount of hindered amine compounds (B-5~B-7) having a melting point below 90°C as shown in Table 2 and 3 was calendered similarly as in Application Example 1 into sheets, and evaluation results are given as Comparative Examples 2-4 in Table 4. Also, the polyester elastomer compounded with hindered amine compound (B-5) as well as hindered phenol compound (C-1); hindered phenol compound (C-1) and phosphite compound (D-1); hindered phenol compound (C-1), phosphite compound (D-1), and benzophenone compound (E-1) in the same amounts was calendered similarly as in Application Example 1 into sheets, and evaluation results are given as Comparative Examples 5-7 in Table 4.

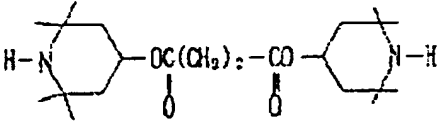
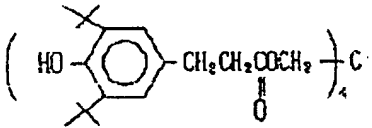
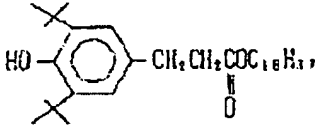
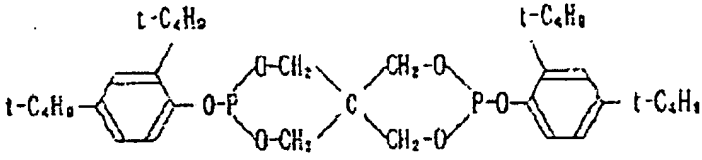
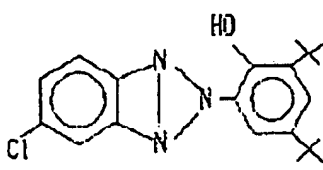
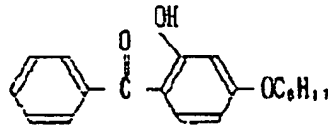
[0048]
Table 2

Table 2

Additive	Structure	Melting point (°C)
B-1		148-150
B-2		130-140
B-3	<p>R: H 又は</p>	130-140
B-4		135-140
B-5		55-70
B-6		72-79

[0049]
Table 3

Table 3

Additive	Structure	Melting point (°C)
B-7		81-85
C-1		110-125
C-2		50-55
D-1		165
D-2	$(n-C_{12}H_{25}S)_3P$	28-30
E-1		154-158
E-2		48

[0050]

Table 4

Table 4

	Polyester elastomer	Additives				Calender processability				Weather resistance	Heat resistance
		(B)	(C)	(D)	(E)	Roll lubricity retention time (min)	Sheet peelability	Plate-out	Surface appearance	Time until crack formation (h)	Time needed to lose one-half of elongation at break (h)
Application Example 1	A-1	B-1				51	5	4	Good	870	102
Application Example 2	A-1	B-2				> 60	5	5	Good	> 1000	76
Application Example 3	A-1	B-3				48	5	3	Good	> 1000	74
Application Example 4	A-1	B-4				52	5	4	Good	810	85
Application Example 5	A-1	B-1	C-1			48	5	3	Good	740	215
Application Example 6	A-1	B-1	C-1	D-1		> 60	5	5	Good	> 1000	266
Application Example 7	A-1	B-1	C-2	D-1		> 60	5	5	Good	830	255
Application Example 8	A-1	B-2	C-1	D-1	E-1	> 60	4	4	Good	> 1200	182
Application Example 9	A-1	B-2	C-2	D-2	E-2	58	5	4	Good	> 1000	202
Comparative Example 1	A-1	—				50	5	4	Good	< 100	64
Comparative Example 2	A-1	B-5				< 1	—	1	—	—	—
Comparative Example 3	A-1	B-6				12	—	2	Poor	—	85
Comparative Example 4	A-1	B-7				18	—	2	Somewhat poor	720	63
Comparative Example 5	A-1	B-5	C-1			< 1	—	1	—	—	—
Comparative Example 6	A-1	B-5	C-1	D-1	E-1	11	—	2	Poor	—	120
Comparative Example 7	A-1	B-5	C-2	D-1	E-1	13	—	2	Somewhat poor	> 1000	98

[0051]

Application Examples 10-15

Polyester elastomer A-2 obtained in Reference Example 2 was used in place of polyester elastomer A-1, fluoro-resin powder (Teflon K10, product of Mitsui Dupont Fluorochemicals Co.) was used as a processing aid, the calender molding temperature was changed to 170°C, and additive systems of Application Examples 1-9 were used to obtain calender sheets. Evaluation results of the sheets are given in Table 5.

[0052]

Comparative Examples 8-14

Polyester elastomer A-2 obtained in Reference Example 2 was used, fluoro-resin powder (Teflon K10, product of Mitsui Dupont Fluorochemical Co.) was used as a processing aid, the calender molding temperature was changed to 170°C, and additive systems of Comparative Examples 1-7 were used to obtain calender sheets. Evaluation results of the sheets are given in Table 4 [sic; 5].

[0053]

Table 5

Table 5

	Polyester elastomer	Additives				Calender processability				Weather resistance	Heat resistance
		(B)	(C)	(D)	(E)	Roll lubricity retention time (min)	Sheet peelability	Plate-out	Surface appearance	Time until crack formation (h)	Time needed to lose one-half of elongation at break (h)
Application Example 10	A-2	B-1				59	4	4	Good	650	190
Application Example 11	A-2	B-2				50	5	4	Good	720	144
Application Example 12	A-2	B-4				52	4	4	Good	650	148
Application Example 13	A-2	B-1	C-1			61	5	5	Good	590	220
Application Example 14	A-2	B-1	C-2	D-1		> 60	5	5	Good	720	310
Application Example 15	A-2	B-2	C-3	D-1	E-1	> 60	4	4	Good	> 1000	235
Comparative Example 8	A-2	—				55	5	4	Good	< 100	135
Comparative Example 9	A-2	B-5				5	—	1	Poor	—	—
Comparative Example 10	A-2	B-6				2	—	1	Poor	—	—
Comparative Example 11	A-2	B-7				6	—	1	Poor	—	—
Comparative Example 12	A-2	B-5	C-1			10	—	2	Poor	—	170
Comparative Example 13	A-2	B-5	C-1	D-1	E-1	16	—	2	Somewhat poor	830	234
Comparative Example 14	A-2	B-5	C-2	D-1	E-1	21	2	2	Somewhat poor	770	201

[0054]

Results in Tables 2-5 show that compared with cases involving no addition of additives (Comparative Example 1 and Comparative Example 8), the calenderable polyester elastomer compositions of the present invention (Application Examples 1-15) with the addition of select high-melting hindered amine compounds have a significantly improved calender processability while a high weather resistance is maintained and molded products have an excellent surface appearance and heat resistance, while such characteristics are synergetically improved by adding other additives such as hindered phenol compounds, phosphite compounds and/or thiophosphite compounds, and benzotriazole compounds together with the hindered amine compounds.

[0055]

On the other hand, when hindered amines with melting points below 90°C were added (Comparative Examples 2-7, 9-14), the calender processability was poor, and even when other additives were additionally added, the calender processability did not improve.

[0056]

Effects of the invention

As explained above, the calenderable polyester elastomer compositions of the present invention can be greatly improved with respect to their calender processability while a high weather resistance is maintained. The compositions can be calendered without sticking or adhering to the rolls to form sheets and films with an excellent surface appearance and heat resistance.

[0057]

Therefore, according to the present invention, polyester elastomer applications are expected to expand further.